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Vertically Aligned Manganese-doped ZnO Nanorods Synthesized on Glassy Carbon Electrode for Detection of Colorants in Soft Drinks

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Synthetic dyes in foods are chemical added to soft drinks and foods during processing or manufacturing. It is very important to monitor artificial colorants in foods due to their potential harm to humans. Herein, sensitive and novel electrochemical sensor based on manganese-doped ZnO (MZO) nanorods was prepared by one step electrochemical method on glassy carbon electrode (GCE) to determine a synthetic food colorant. Differential pulse voltammetry and cyclic voltammetry were applied to study the electrochemical performance of sunset yellow. As-prepared MZO/GCE was directly used as electrochemical sensor for amperometric determination of sunset yellow, which indicated a high sensitivity of 7.75 μA/μM and a low detection limit of 5.2 nM. This proposed technique exhibited good stability, outstanding selectivity, and satisfactory reproducibility and repeatability, and also had been applied to simultaneously detect sunset yellow in soft drinks with suitable results.

Keywords: Artificial colorants; Soft drinks; Differential pulse voltammetry; Manganese-doped ZnO nanorods; Sunset yellow; Electrochemical sensor

1. INTRODUCTION

The Food Standards Agency has suggested that controlling food additives as an important technique to verify food products because of its high risk to human health[1, 2]. Sunset yellow is widely used as an artificial color in food preparation to make food more appealing and attractive[3]. However, reports indicate that having a diet of sunset yellow changes the neurobehavioral and reproductive parameters [4]. Furthermore, yellow sunset had shown that it can significantly reduce thymus weight by changing the number of monocytes[5, 6].Therefore, the sunset yellow content in the food should be completely controlled, and the determination of the sunset yellow in a fast and simple way is remarkable.

Some analytical techniques such as electrochemical, high-performance liquid chromatography (HPLC)and spectroscopy sensors were recommended for analysis of dye specimens in food [7, 8]. Meanwhile, the HPCL method have been used in many compounds over the years due to their widespread use [9]. Hard operation, expensive, long-time analysis and using toxic solvents are major disadvantage of HPLC technique. Therefore, electrochemical sensors have been developed in recent years to analyze food additives because of their good sensitivity and easy operation [10, 11]. Moreover, the ability of the electrochemical sensor to become portable kits and to determine the electroactive material at the nanomolar level, contributes to their significant growth in the industry[12].

In this case, nanomaterial-modified electrodes are widely used. Zinc oxide (ZnO) nanostructures have efficient electrocatalytic and electronic properties, and their films reveal significant enhancement in surface than the unmodified electrodes, that increases the sensor sensitivity [13, 14]. The electrocatalytic property of ZnO is extensively accepted and has been used in different concepts of studies [15]. Some reports have shown that doped ZnO by transition metal such as Cu, Ag, Mn and Au increases the electrocatalytic activity [16, 17].

Here, we report the fabrication of Mn doped ZnO-modified glassy carbon electrode (MZO-GCE) using a facile electrochemical method for monitoring sunset yellow in food samples. The electrochemical behavior of sunset yellow on the MZO-GCE electrode was studied by differential pulse voltammograms (DPV) and cyclic voltammograms (CV) analysis. Furthermore, the MZO-GCE was used to evaluate commercial soft drinks as real sample.

2. MATERIALS AND METHOD

The surface of glassy carbon electrode (GCE) was polished by 0.1 μm alumina slurry and washed with DI water. For preparation of MZO-GCE electrode, the GCE were coated by 50 nm ZnO seed layer using a magnetron sputter. ZnO nanorods were synthesized by two electrode electrochemical technique. Zinc nitrate hydrate (25 mM) and hexamethylenetetramine (25 mM) were dissolved in 50 ml DI water under stirring. To synthesize Mn-doped ZnO nanorods on GCE, 1 M Zinc acetate dihydrate, 1 M hexamethylenetetramine and manganese tetrachloride (5 mol%) were dissolved separately in 50 ml DI water. Then, ammonia was added to prepared solution of 10 pH adjustment. This solution was transferred into the electrochemical cell. The ZnO seed layer coated on the GCE and Pt was applied as cathode and anode electrodes, respectively. MZO nano rods was produced at one hour growth time, 0.5 mA/cm^2 current density and 95 ^{o}C temperature. The prepared samples were washed and dried by DI water and nitrogen gas, respectively.

FEI Sirion 200 scanning electron microscopy (SEM) and X-ray powder diffraction (XRD, PAN alytical, X'Pert PRO) analysis were employed to evaluate the morphological and structural properties of the MZO-GCE. Electrochemical measurements of sunset yellow were done in 0.1 M phosphate buffer (PB) solution with pH 7.0. Differential pulse voltammograms (DPV) and cyclic voltammograms (CV) were carried out in 0.1V-0.9V potential range. The conditions of DPV operating were a 0.05V pulse amplitude, a 0.2spulse period and 0.004 V potential increment at room temperature. The sunset yellow were accumulated on the MZO-GCE for 2 min at open circuit potential. Then, the DPV results were recorded after 20s of equilibration. Soft drinks as real samples were purchased at local grocery stores and degassed with mild stirring for 30 min.

3. RESULTS AND DISCUSSION

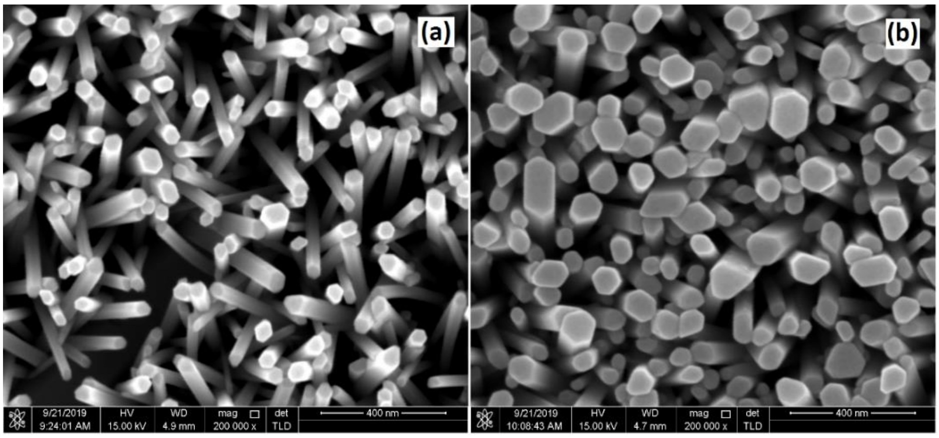

Figure 1. The surface morphology of (a) ZO-GCE and (b) MZO-GCE samples.

Figure 1 shows the surface morphology of ZO-GCE and MZO-GCE samples. The hexagonal shape of ZnO and its growth direction of perpendicular to the GCE surface can be observed in figure 1a. As shown in figure 1b, the diameters of ZnO doped by Mn ions significantly increase. The MZO diameters were ranged from50 nm to 120 nm. Furthermore, the number of nanorods were enhanced by doping process. The effects of doping on ZnO morphology had been reported[18]. Due to the increase in length, diameter and amount of nanorods observed on the surface of electrode, it can be concluded that the increase in growth of ZnO crystal was influenced by the elements of manganese.

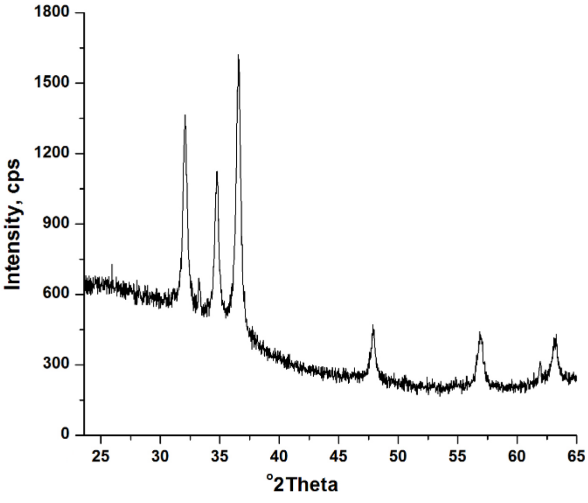

Figure 2. XRD patterns of MZO-GCE.

The XRD pattern of MZO-GCE is revealed in figure 2. It is observed that there are only peaks related to the hexagonal structure of Wurtzite ZnO (JCPDS 36-1451), no secondary peaks of possible impurities such as manganese oxide [19].

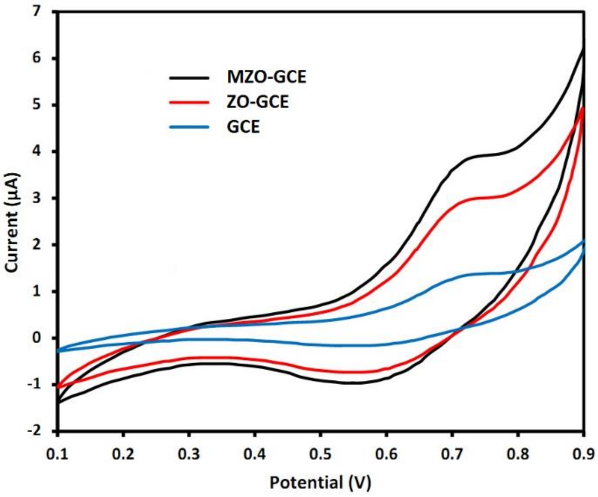

Figure 3. Cyclic voltammograms recorded by GCE, ZO-GCE and MZO-GCE electrodes in 0.1M PB solution, including 0.5 mM sunset yellow at 50 mVs^{-1} scan rate

The cyclic voltammograms (CV) recorded by GCE, ZO-GCE and MZO-GCE electrodes were carried out between 0.1 and 0.9V using 50 mVs^{-1} scan rate in 0.1M PB solution, including 0.5 mM sunset yellow. A single peak of oxidation was found at 0.72 V in GCE. As shown in figure 3, the irreversible behavior of GCE electrode was changed by the modified MZO-GCE. A pair of well-defined redox peaks had appeared at 0.72V and 0.58V for MZO-GCE, which indicated that the sunset yellow was initially adsorbed on the MZO and then oxidized. Moreover, the current value had increased in modified electrode which revealed that the MZO-GCE had electrocatalytic behavior to the sunset yellow oxidation [20].

In order to further study of the electrochemical oxidation procedure of sunset yellow at MZO-GCE, the scan rate effect was investigated by CVs in a pH 8 PB solution with varying scan rates between 0.05 to 1.0 Vs^{-1} (Figure 4a). As shown in figure 4b, the intensity of cathodic and anodic peak currents were linearly proportional with the scan rates at the defined range, indicating the oxidation of sunset yellow is an adsorption-controlled procedure[21, 22]. As scan rate increased, the peak potentials of cathodic and anodic began to expand and shifted to negative and positive directions which can be attributed to the electrochemical process kinetics. Certainly, it took a lot of over potential to keep enough flux from electrons to be transferred into electrode surface since the period of CV tests were reduced to be comparable to electron transmission kinetics [23].

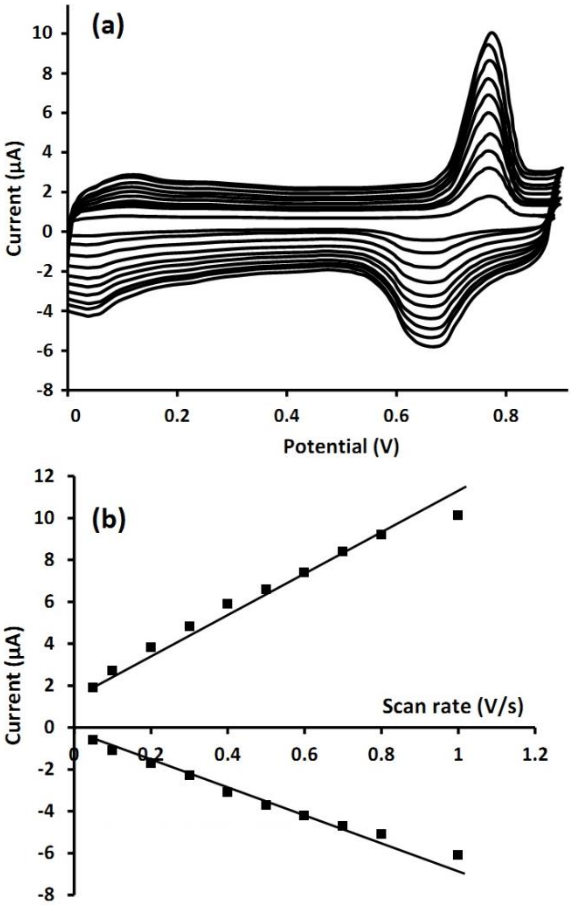

Figure 4. CVs of 10 µML^{-1} sunset yellow in 0.1M PB solution at pH 8.0 in various scan rates

DPV is a highly selective and sensitive electrochemical technique which is used for quantitative analysis of colorants [24]. Figure 5a indicates the DPV response of MZO-GCE electrode to the different concentrations of sunset yellow in 0.1 M PB solutions. It can be noted that the MZO-GCE obtained a steady-state current, revealing the prepared sensor had a rapid response to sunset yellow. Figure 5b shows the diagram of peak currents versus sunset yellow concentration that indicated the linear response of electrochemical sensor for detection of sunset yellow. The detection limit and sensitivity of the sensor were determined as 5.2 nM and 7.75 µA/µM, respectively. The superior performance of MZO-GCE electrode can be related to synergistic effect of doping structure, catalytic activity and good electrical conductivity of Mn doped ZnO nanorods [25, 26]. Table 1 exhibits the comparison of various methods to detect the sunset yellow in previous studies. The suggested technique in this work indicated a relatively low detection limit and high sensitivity in sunset yellow which can be applied in practical specimens.

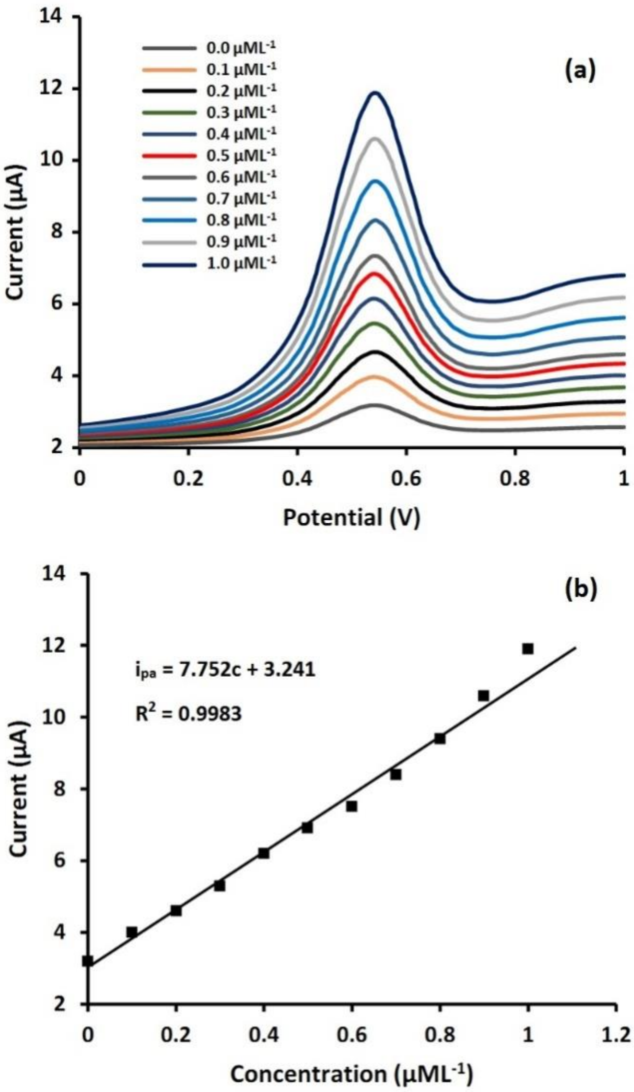

Figure 5. (a) DPV response of MZO-GCE electrode to successive injection of 0.1 μM sunset yellow in 0.1 M PB solution at pH 8.0 and scan rate of 50 mV s^{-1} (b) Diagram of peak currents vs. sunset yellow concentration.

Table 1. Comparison of techniques for detection of sunset yellow.

Ref.	Electrode	Method	Detection limit	Sensitivity
[27]	MWCNT/GCE	DPV	22 nM	0.046 μA/μM
[28]	MWCNTS-IL/GCE	DPV	100 nM	0.39 μA/μM
[29]	β-CD-PDDA-Gr/Gc-RDE	DPV	12.5 nM	0.056 μA/μM
[30]	RGO/MWCNT	DPV	25 nM	0.46μA/μM
[31]	IL-rGO/GCE	DPV	4 nM	5.0 μA/μM
This work	MZO-GCE	DPV	5.2 nM	7.75 μA/μM

The prepared MZO-GCE electrode was used to determine the sunset yellow in different soft drinks to consider its feasibility and practicability. The specimens were attained from local grocery stores. Then, 20 µL of the specimen solution was directly added into 0.1M PB solution (pH 8). The DPV method was used as an analytical procedure. The concentration of sunset yellow was evaluated by standard addition technique and four parallel determinations were done for each specimen solution. The results were summarized in Table 2. The recovery of sunset yellow detections were between 97.2% and 109.4%, which revealed that the MZO-GCE can be applied for feasible and accurate determination of sunset yellow in test samples.

Table 2. Determination of sunset yellow concentrations in soft drinks

Soft drinks	Added (µM)	Found (µM)	Recovery (%)
1	8.00	7.87	97.2
2	4.00	3.91	98.3
3	2.00	2.17	109.4
4	1.00	1.01	101.1

4. CONCLUSIONS

The Food Standards Agency has suggested controlling food additives as an important technique to verify food products because of its high risk to human health. In this study, a sensitive and novel electrochemical sensor based on MZO nanostructures was prepared by a simple electrochemical method on GCE substrate for determination of a synthetic food colorant. DPV and CV analysis were applied to study the electrochemical performance of sunset yellow. As-prepared MZO/GCE was directly used as electrochemical sensor for amperometric determination of sunset yellow, which indicated a high sensitivity of 7.75 µA/µM and a low detection limit of 5.2 nM. This proposed technique exhibited good stability, outstanding selectivity, and satisfactory reproducibility and repeatability, and also has been applied to simultaneously detect sunset yellow in soft drinks with suitable results. The recovery of sunset yellow detections were between 97.2% and 109.4%, which revealed that the MZO-GCE can be applied for feasible and accurate determination of sunset yellow in test samples.

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References

1. M. Iammarino, R. Marino and M. Albenzio, *International Journal of Food Science & Technology*, 52 (2017) 851.
2. Z. Shamsadin-Azad, M.A. Taher, S. Cheraghi and H. Karimi-Maleh, *Journal of Food Measurement and Characterization*, 13 (2019) 1781.
3. L. Magerusan, F. Pogacean, M. Coros, C. Socaci, S. Pruneanu, C. Leostean and I.O. Pana, *Electrochimica Acta*, 283 (2018) 578.

4. M. Arvand, M. Zamani and M.S. Ardaki, *Sensors and Actuators B: Chemical*, 243 (2017) 927.
5. M.M. Hashem, A.H. Atta, M.S. Arbid, S.A. Nada and G.F. Asaad, *Food and Chemical Toxicology*, 48 (2010) 1581.
6. Y. Yang, S. Zhang and S. Ren, *International Journal of Electrochemical Science*, 14 (2019) 7684.
7. A. Peña-Gonzalez, O. García-Beltrán and E. Nagles, *International Journal of Electrochemical Science*, 13 (2018) 5005.
8. H. Karimi-Maleh and O.A. Arotiba, *Journal of colloid and interface science*, 560 (2020) 208.
9. M.A. Hasan, S.T. Hashim, S.E. Abid and J.S. Bajlan, *Current Research in Microbiology and Biotechnology*, 6 (2018) 1460.
10. A. Samide, G.E. Iacobescu, B. Tutunaru and C. Tigae, *International Journal of Electrochemical Science*, 12 (2017) 2088.
11. H. Karimi-Maleh, K. Cellat, K. Arıkan, A. Savk, F. Karimi and F. Şen, *Materials Chemistry and Physics*, 250 (2020) 123042.
12. M. Bijad, H. Karimi-Maleh, M. Farsi and S.-A. Shahidi, *Food analytical methods*, 10 (2017) 3773.
13. M. Heydari, S.M. Ghoreishi and A. Khoobi, *Food chemistry*, 283 (2019) 68.
14. F. Husairi, J. Rouhi, K. Eswar, C.R. Ooi, M. Rusop and S. Abdullah, *Sensors and Actuators A: Physical*, 236 (2015) 11.
15. R. Dalvand, S. Mahmud and J. Rouhi, *Materials Letters*, 160 (2015) 444.
16. B.Y. Sahyar, M. Kaplan, M. Ozsoz, E. Celik and S. Otles, *Bioelectrochemistry*, 130 (2019) 107327.
17. A. Mahmoud, M. Echabaane, K. Omri, L. El Mir and R.B. Chaabane, *Journal of Alloys and Compounds*, 786 (2019) 960.
18. M. Samadi, M. Zirak, A. Naseri, E. Khorashadizade and A.Z. Moshfegh, *Thin Solid Films*, 605 (2016) 2.
19. J. Rouhi, C.R. Ooi, S. Mahmud and M.R. Mahmood, *Electronic Materials Letters*, 11 (2015) 957.
20. P.S. Dorraji and F. Jalali, *Food chemistry*, 227 (2017) 73.
21. Q. He, J. Liu, X. Liu, Y. Xia, G. Li, P. Deng and D. Chen, *Molecules*, 23 (2018) 2130.
22. J. Rouhi, M.H. Mamat, C.R. Ooi, S. Mahmud and M.R. Mahmood, *PLoS One*, 10 (2015) e0123433.
23. E.P. Randviir, *Electrochimica Acta*, 286 (2018) 179.
24. K. Ghanbari, M. Roushani, F. Farzadfar, H.C. Goicoechea and A.R. Jalalvand, *Chemometrics and Intelligent Laboratory Systems*, 189 (2019) 27.
25. N.A. Putri, V. Fauzia, S. Iwan, L. Roza, A.A. Umar and S. Budi, *Applied Surface Science*, 439 (2018) 285.
26. F. Tahernejad-Javazmi, M. Shabani-Nooshabadi and H. Karimi-Maleh, *Composites Part B: Engineering*, 172 (2019) 666.
27. M. Wang, Y. Gao, Q. Sun and J. Zhao, *Journal of The Electrochemical Society*, 161 (2014) B297.
28. M.R. Majidi, R.F.B. Baj and A. Naseri, *Food analytical methods*, 6 (2013) 1388.
29. X. Ye, Y. Du, D. Lu and C. Wang, *Analytica chimica acta*, 779 (2013) 22.
30. X. Qiu, L. Lu, J. Leng, Y. Yu, W. Wang, M. Jiang and L. Bai, *Food chemistry*, 190 (2016) 889.
31. L. Zhao, F. Zhao and B. Zeng, *Electrochimica Acta*, 115 (2014) 247.